

SUBSTRATE, SUCH AS A GLASS SUBSTRATE, WITH A
 HYDROPHOBIC SURFACE AND IMPROVED DURABILITY OF
 HYDROPHOBIC PROPERTIES

- 5 The present invention relates to a substrate, especially a glass substrate, the surface of which has been rendered hydrophobic, with improved durability of the hydrophobic properties.
- 10 Hydrophobic properties are sought for windows and windshields in the transport field, in particular for motor vehicles and aircraft, and also for glazing in the building industry.
- 15 For applications in the transport field, rain-repellent properties are sought, the water droplets on windshields thus having to easily roll off the glass wall so as to be removed, for example when the vehicle is in motion due to the effect of the air or wind, and
- 20 to do so with the purpose of improving visibility and, consequently safety, or for facilitating cleaning, or for easily defrosting, etc.

For applications in the building field, the aim is

25 essentially to make cleaning easier.

For this purpose, the aim is to have an angle of contact of a water droplet with the substrate that is greater than 60° or 70°, the water droplet having not

30 to be flattened or spread out. This is because glazing is said to be functional as long as this angle is greater than 60° in the case of aircraft, and greater than 70° in the case of automobiles. However, in practice this angle should in all cases exceed 90°, the

35 ideal being to obtain droplets that roll off, allowing the water to be removed so quickly as to be able to dispense as far as possible with windshield wipers in the automotive field.

Moreover, the improvement in hydrophobic properties thus sought must not be to the detriment of the preservation of the other properties, such as
5 resistance to mechanical stresses: resistance to shear friction (standardized Opel test, carried out dry), abrasion resistance (Taber test), resistance to wiping by wipers (test simulating the cycles of wiper action); resistance to environmental stresses (WOM test of UVA
10 resistance, or Xenon test; QUV test of UVB resistance for aircraft; NSS (neutral salt spray) resistance test; resistance to chemical stresses: test of resistance to acid and basic detergents; and the optical properties.

15 To render a glass hydrophobic it is known to coat it with a dense silica mineral layer serving as primer for the grafting of molecules having hydrophobic properties, such as fluorosilane molecules. Thus, European patent EP 0 545 201 describes the application
20 of a dense SiO_2 layer applied by magnetron sputtering, said SiO_2 layer being subsequently coated with a hydrophobic agent.

The filing company has discovered that the hydrophobic
25 properties of such a structure can be further improved, in particular in their durability, with the other properties mentioned above being at least maintained, or even sometimes improved, if the coating of molecules having hydrophobic properties is applied while this
30 layer is in an activated surface state, this activation being able to be produced either by the actual conditions under which the mineral layer is deposited, or by a specific activation treatment.

35 Thus, the mineral layer (which is the sublayer in the resulting final structure) may be deposited by vacuum sputtering, especially magnetron sputtering, under conditions that allow the layer to be left in an

unstable surface state, with the hydrophobic coating being applied while the surface is still in this state (generally applied immediately), or by a specific activation treatment (plasma excitation, etc.).

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A first subject of the present invention is therefore a substrate, at least one part of the surface of which has been rendered hydrophobic, having for this purpose a hydrophobic surface structure comprising an essentially mineral silicon-containing sublayer and an outer layer of hydrophobic agent grafted onto said sublayer, characterized in that said sublayer has received the outer layer of hydrophobic agent although it had a surface that was in an activated state before being brought into contact with said hydrophobic agent.

The term "activated" is understood to mean that said surface has undergone a treatment which has modified its electrostatic state (by production of charges) and/or its chemical state (creation or destruction of chemical functional groups), in order to increase the reactivity of said surface, which treatment may go as far as tearing the material of the surface, thus creating irregularities. Moreover, as will be indicated below, the layer of silicon-containing mineral material that will constitute the sublayer in the final structure may be obtained under conditions in which it is directly in the activated state.

30 The sublayer may be a hard sublayer.

The substrate is especially formed by, or comprises in its part intended to bear said mineral sublayer, a plate, whether plane or with curved faces, of monolithic or laminated glass, of glass-ceramic or of a hard thermoplastic, such as polycarbonate. The glass may be a toughened glass. An example of a curved plate is a windshield. This may be in the assembled state.

The sublayer of the hydrophobic coating may form part of the substrate, the latter being formed by a plate, whether plane or with curved faces, of monolithic or laminated glass or of glass-ceramic, the composition of which, at least on the surface, corresponds to that of the essentially mineral silicon-containing sublayer. An example of a substrate having such an integrated sublayer is a glass dealkylized at least on its surface. International applications WO-94/07806 and WO-94/07807 describe this technology.

The silicon-containing sublayer is especially formed by a compound chosen from SiO_x , where $x \leq 2$, SiOC , SiON , SiOCN and Si_3N_4 , it being possible for hydrogen to be combined in all proportions with SiO_x , where $x \leq 2$, SiOC , SiON and SiOCN . It may also contain aluminum, in particular up to 8% by weight, or carbon, Ti, Zr, Zn and B.

Mention may also be made of sublayers consisting of scratch-resistant lacquers, such as polysiloxanes, which have been applied as coating on polycarbonate substrates.

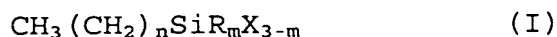
The silicon-containing sublayer when its surface is in the activated state has a thickness of between 20 nm and 250 nm, especially between 30 nm and 100 nm and in particular between 30 nm and 75 nm. It may have an RMS roughness of between 0.1 nm and 40 nm, in particular between a few nm and 30 nm. It may have an actual developed area at least 40% greater than the initial plane area. Under an SEM microscope, said sublayer may have the appearance of pumistone or of islands.

Moreover, the silicon-containing sublayer when its surface is in the activated state advantageously has a hardness such that it does not delaminate after 100

revolutions, and preferably up to 200 revolutions, in the Taber test.

The hydrophobic agent may be chosen from:

- 5 (a) alkylsilanes of formula (I):

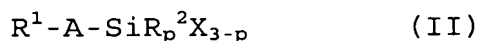


in which:

- n ranges from 0 to 30, more particularly from 0 to 18;
- 10 - m = 0, 1, 2 or 3;
- R represents an optionally functionalized organic chain; and
- X represents a hydrolyzable residue, such as an OR^0 residue, where R^0 represents hydrogen;
- 15 or a linear, branched or cyclic, especially $\text{C}_1\text{-C}_8$, alkyl residue; or an aryl residue; or such as a halo, for example chloro, residue;

- (b) compounds with grafted silicone chains, such as for example $(\text{CH}_3)_3\text{SiO}[\text{Si}(\text{CH}_3)_2\text{O}]_q$, with no
- 20 specific limitation as regards the chain length (value of q) and the method of grafting;

- (c) fluorosilanes, such as those of formula (II):



in which:

- 25 - R^1 represents an especially $\text{C}_1\text{-C}_9$ monofluoroalkyl, oligofluoroalkyl or perfluoroalkyl residue; or a monoaryl, oligoaryl or perfluoroaryl residue;
- A represents a hydrocarbon chain, optionally
- 30 interrupted by a heteroatom such as O or S;
- R^2 represents a linear, branched or cyclic, especially $\text{C}_1\text{-C}_8$, alkyl residue, or an aryl residue;
- X represents a hydrolyzable residue, such as
- 35 an OR^3 residue, where R^3 represents hydrogen or a linear, branched or cyclic, especially $\text{C}_1\text{-C}_8$, alkyl residue; or an aryl residue; or such as a halo, for example chloro, residue;

and
- p = 0, 1 or 2.

An example of an alkylsilane of formula (I) is
5 octadecyltrichlorosilane (OTS).

The preferred hydrophobic agents are fluorosilanes (c),
in particular those of formula (II), particular
examples of the latter being those of formula:

10
$$\text{CF}_3 - (\text{CF}_2)_n - (\text{CH}_2)_2 - \text{Si}(\text{R}^4)_3$$

in which:

- R^4 represents a lower alkyl residue; and
- n is between 7 and 11.

15 The layer of hydrophobic agent has for example a
thickness of between 1 and 100 nm, preferably between 2
and 50 nm.

The layer of fluorosilane may have a weight per unit
20 area of grafted fluorine of between $0.1 \mu\text{g}/\text{cm}^2$ and
 $3.5 \mu\text{g}/\text{cm}^2$, in particular between $0.2 \mu\text{g}/\text{cm}^2$ and
 $3 \mu\text{g}/\text{cm}^2$.

The subject of the present invention is also a process
25 for manufacturing a substrate as defined above,
characterized in that a coating layer of hydrophobic
agent is deposited, in at least one pass, on the
surface of a silicon-containing mineral layer formed at
least partly on the surface of the substrate, said
30 deposition of the hydrophobic agent taking place while
said surface is in the activated state.

An activated surface of the silicon-containing mineral
layer may be obtained by depositing it under conditions
35 in which its surface is obtained directly in the
activated state. This is what occurs if a silicon-
containing layer is deposited, cold, by PECVD (plasma
enhanced chemical vapor deposition) or by magnetron

and/or ion-beam sputtering.

This is because, in such processes, the growth of the layer takes place using reactive species (ions, radicals, neutrals, etc.) which combine to form the coating. The surface of the coating is therefore by nature in an off-equilibrium state. In addition, this layer may be directly in contact with the plasma gas during growth, which will further increase the activity of the surface and its reactivity (as in the PECVD process).

It is also possible to obtain an activated surface of the silicon-containing mineral layer by carrying out an activation treatment in at least one pass.

Advantageously, the hydrophobic agent is deposited within the shortest possible time, preferably between 1 second and 15 minutes, after the activated surface has been obtained.

An activation treatment may be carried out under conditions that do not go as far as etching, by the use of a plasma or an ionized gas, at reduced or atmospheric pressure, chosen from air, oxygen, nitrogen, argon, hydrogen, ammonia and mixtures thereof, or by the use of an ion beam.

It is also possible to carry out an activation treatment under conditions that allow a silicon-containing layer to be etched, by the use of a plasma of at least one fluorine-containing gas chosen from SF_6 , CF_4 , C_2F_6 and other fluorinated gases, where appropriate combined with oxygen, it being possible for the oxygen to represent up to 50% by volume of the etching plasma.

Moreover, according to the present invention, the activation carried out under conditions that allow the

silicon-containing layer to be etched by an activation treatment, which does not cause additional etching but does still modify the chemical nature and/or the electrostatic state of said layer, may be monitored.

5

The silicon-containing layer may be deposited, cold, on the substrate by vacuum cathode sputtering, preferably magnetron sputtering and/or ion beam sputtering, or by low-pressure or atmospheric-pressure PECVD, or else
10 deposited hot by pyrolysis.

As examples of the deposition of the SiO₂ sublayer, the following method of implementation may be mentioned, in which: a layer of SiO₂ is deposited on bare glass or on
15 an assembled windshield by PECVD, using a mixture of an organic or nonorganic, silicon-containing precursor, such as SiH₄, hexamethyldisiloxane (HMDSO), tetraethoxysilane (TEOS) and 1,1,3,3-tetramethyldisiloxane (TMDSO), and an oxidizer (O₂, NO₂,
20 CO₂), the subsequent activation being carried out in the same chamber or in a separate chamber.

The hydrophobic agent layer may be deposited by wiping-on, evaporation or spraying of a solution containing
25 the hydrophobic agent, or by dipping, spin-coating, flow-coating, etc., using a solution containing the hydrophobic agent.

To manufacture glazing with a hydrophobic coating
30 according to the present invention, it will be possible to use *inter alia*, one of the following three general methods:

(1) the sublayer is deposited on the glass on a glass manufacturing line using the "float" process
35 while the glass is being supported by the bath of molten tin, or in a subsequent step, that is to say on leaving the bath of molten tin, the conversion operations are then carried out, such as bending,

toughening and/or assembling, especially by lamination, in order to obtain plates of glass made up from one or more sheets coated with the sublayer on at least one face, the sublayer or sublayers supported by said
5 plates are then activated and, finally, a functionalization by the hydrophobic agent of the sublayer or sublayers thus activated is carried out. The sublayer is generally deposited by PECVD or magnetron sputtering;

10 (2) sheets of glass are manufactured by the float process, said glass sheets are then converted by operations such as bending, toughening and/or assembling, especially lamination, in order to obtain plates of glass made up from one or more sheets, the
15 sublayer is then deposited on at least one face of the plates thus obtained, and the sublayer or sublayers are then activated, followed by the functionalization by the hydrophobic agent of the sublayer or sublayers thus activated;

20 (3) the sublayer is deposited on at least one face of glass sheets obtained upon leaving the float process, these sheets thus coated with the sublayer or sublayers are converted, limiting the techniques used to those that do not damage said sublayer(s) (thereby
25 excluding bending and toughening as conversion operations, but allowing assembling, especially by lamination), and the sublayer or sublayers are then activated, followed by the functionalization by the hydrophobic agent of said sublayer or sublayers thus
30 activated.

The present invention also relates to rain-repellent glazing comprising a substrate as defined above or prepared by the process as defined above. Mention may
35 be made of glazing for buildings, including glazing for shower cubicles, glass for electrical household appliances, especially glass-ceramic hobs, glazing for transport vehicles, especially for automobiles and

aircraft, in particular for windshields, side windows, rear windows, wing mirrors, sunroofs, headlamp and rear light optics, and ophthalmic lenses.

5 The following examples illustrate the present invention without however limiting the scope thereof. In these examples, the following abbreviations have been used:

PECVD: plasma enhanced chemical vapor
deposition;
10 SEM: scanning electron microscopy;
AFM: atomic force microscopy; and
AWR: aviation wiping rig.

EXAMPLE 1: Substrate having a hydrophobic surface
15 according to the invention with a silica
sublayer formed by PECVD

(a) Formation and characterization of the hard silica
sublayer

20

A thin silica (SiO_2) layer was deposited on a clean glass (measuring $300 \times 300 \text{ mm}^2$) in a low-pressure PECVD reactor. Before each experiment, the residual vacuum reached in the chamber was at least 5 mPa (5×10^{-5}
25 mbar). The gas mixture was then introduced into the chamber. The gases used were pure silane (SiH_4), nitrous oxide (N_2O) and dilution helium, the respective flow rates of which were 18 sccm, 60 sccm and 60 sccm. The total pressure in the reactor was then set at 9.99 Pa
30 (75 mTorr). In equilibrium, the plasma was struck by biasing the gas diffuser with an average radiofrequency (13.56 MHz) power of 190 W (bias voltage: $\sim 45 \text{ V}$). The temperature of the substrate was kept at 25°C . The thickness of silica thus deposited after 270 s was
35 about 50 nm.

The surface state of the PECVD silica observed in SEM was characterized by small grains about twenty

nanometers in size, which, in places, formed circular or elongate areas of additional thickness that were hollow at their center.

5 The hardness of the silica obtained was characterized using the following two tests:

- firstly, the layer underwent an abrasion treatment, during which the haze was measured according to the standard ISO 3537; the abrasion was of the Taber
10 type, carried out by means of a CS10F abrasive wheel with an applied force of 4.9 N (500 g). The degree of abrasion was denoted by the number of Taber revolutions. The measured haze values are given in Table 1 below; and

15 - secondly, the hardness of the silica was assessed by the Airco rating, the value being 10 - 0.18R in which R is the number of scratches, after a given number of Taber revolutions, in a frame measuring 2.54 cm × 2.54 cm, visible on a photograph with a ×50
20 magnification. The Airco ratings are also given in Table 1 below.

Table 1: Characterization of the SiO₂ sublayer

State of abrasion:	Taber revolutions			
	50	100	200	300
Haze	0.55	1.01	1.58	1.75
Airco	7.48	7.48	6.76	5.86

25

These values characterize a hard SiO₂ layer.

(b) Plasma treatment

30 The SiO₂ layer was then subjected to a plasma treatment.

As in the case of the deposition experiments, a residual vacuum of at least 5 mPa (5×10^{-5} mbar) was again created in the chamber before the reactive gas

mixture was introduced. The gases used for the surface treatment of the silica were C_2F_6 and oxygen, the respective flow rates of which were 120 sccm and 20 sccm. The total pressure in the reactor was then set at 26.66 Pa (200 mTorr). At the equilibrium, the plasma was struck by biasing the gas diffuser with an average radiofrequency (13.56 MHz) power of 200 W (bias voltage: ~ 15 V) for a time of 900 s at room temperature.

10

After 15 minutes of C_2F_6/O_2 plasma treatment, the silica layer was highly etched. Its surface had large blisters a few tens of nanometers in size. The microroughness obtained with this highly aggressive plasma (etching) treatment was characterized by AFM, indicating an apparent roughness on the scale of the fluorosilane molecules subsequently grafted onto the silica.

The main microroughness parameters of the PECVD silica measured by AFM are given in Table 2 below.

20

Table 2

Substrate	ΔZ_{\max}^* (nm)	R_{rms} (nm)	Developed area (2×2 μm^2)	Increase (%)
Flat glass	0.5	~ 0.2	4.1	+ 2.5
SiO_2	10	1.657- 2.116	4.431	+ 10.785
Etched SiO_2	30	5.981- 7.216	5.5	+ 37

* ΔZ_{\max} is the maximum peak/valley amplitude.

25

(c) Application of fluorosilane

After the surface of the PECVD silica had been plasma-

treated, a composition was wiped onto the specimens, the composition having been produced 12 hours beforehand in the following manner (the percentages are in weight):

- 5 - 90% of propanol-2 and 10% of 0.3N HCl were mixed in water; and
- added to the two aforementioned constituents was 2% of the compound of formula $C_8F_{17}(CH_2)_2Si(OEt)_3$ (Et = ethyl).

10

The weights per unit area of fluorine grafted onto the surface of the various sublayers, determined by electron microprobe, were:

- on flat glass (with sol-gel
- 15 SiO_2 primer sublayer): $0.15 \mu g/cm^2$
- on SiO_2 (PECVD): $0.369 \mu g/cm^2$
- on etched SiO_2 (PECVD): $1.609 \mu g/cm^2$.

20 The amount of fluorine grafted onto the etched SiO_2 sublayer is remarkably high.

(d) Characterization of the hydrophobic substrate obtained

25 The characteristics of the hydrophobic substrate obtained were:

- droplet contact angle: $\mu_{water} \geq 105^\circ$;
- optical properties: $T_L = 90.2\%$; $R_L = 8.44\%$;
absorption = 1.36% ; haze = 0.2% ;
- 30 - detachment volumes: $13 \mu l$ at 90° and $22 \mu l$ at 45° (the angles being the angles of inclination of the substrate to the horizontal).

35 Next, the above three types of fluorosilane-grafted substrates were subjected to two types of mechanical tests:

- Taber test using a CS-10F abrasive wheel with a load of $4.9 N$ ($500 g$);

- Opel test according to Building Standard EN 1096-2 of January 2001, consisting in applying, to part of the coated surface 9.4 cm in length - this part being called a track - a felt 14 mm in diameter, 10 mm in thickness and 0.52 g/cm² in density, and a load of 39.22 MPa (400 g/cm²), the felt being subjected to a translational movement (50 to-and-fro movements over the entire track length per minute) combined with a rotation of 6 revolutions/minute (1 cycle = 1 to-and-fro movement).

The results of the Opel and Taber tests on the etched and unetched PECVD layers compared with the flat glass are given in Table 3 below.

Table 3

	Opel (39.22 MPa (0.4 kg/cm ²))	Taber revolutions (CS-10F-4.9 N (500 g))	
		100	300
Control*	95° ± 5°	75° ± 5°	≤ 60°
PECVD SiO ₂	87° ± 2°	95° ± 1°	83° ± 2°
Etched SiO ₂	95° ± 5°	90° ± 1°	74° ± 2°

*Specimen prepared according to Example 5b of EP 799 873 B1.

The 87° value in the Opel test (5000 cycles) for the case of the SiO₂ sublayer is not sufficient.

Only the substrate with an etched SiO₂ sublayer results in a good compromise between the Opel test and the Taber test (100 revolutions).

This substrate was therefore tested in the AWR, consisting in moving an aircraft windshield wiper over it along a 25 cm track in a transverse movement consisting of two to-and-fro movements per second,

under a load of 0.88 N/cm (90 g/cm) with a water spray of 6 l/h.

5 A mean angle of about $80^\circ \pm 10^\circ$ after 1 000 000 cycles was measured, with only 26% of the area not functional ($\mu_{\text{water}} < 60^\circ$). The functionality limit was measured to be 1 400 000 cycles, at which the mean angle was about $70^\circ \pm 10^\circ$ with more than 35% of the area not functional.

10

The substrate was also assessed by the following main accelerated environmental tests:

- WOM or Xenon test: 0.55 W/m² irradiation at 340 nm;
- 15 - QUV: 16 h of UV-B (313 nm) at 70°C + 8 h at 40°C (> 95% residual humidity);
- NSS: exposure at + 35°C, 50 g/l NaCl at 7 pH according to the IEC 60 068 standard, part 2-11 Ka.

20 All the results are given in Table 4.

Table 4

	WOM		QUV		BSN	
	600 h	2000 h	1500 h	3500 h	2 weeks	4 weeks
Control*	$105^\circ \pm 5^\circ$	$95^\circ \pm 3^\circ$	$90^\circ \pm 5^\circ$		$65^\circ \pm 15^\circ$	$65^\circ \pm 15^\circ$
Etched SiO ₂	$104^\circ \pm 5^\circ$	$102^\circ \pm 3^\circ$	$105^\circ \pm 5^\circ$	$95^\circ \pm 3^\circ$	$103^\circ \pm 15^\circ$	$103^\circ \pm 5^\circ$

*Specimen prepared according to Example 5b of
25 EP 799 873 B1.

The etched PECVD sublayers made it possible to maintain, in the QUV test, a $\mu_{\text{water}} > 80^\circ \pm 6^\circ$ after 7000 hours of exposure and a $\mu_{\text{water}} \geq 96^\circ \pm 3^\circ$ after 2800
30 hours of exposure in the WOM.

EXAMPLE 2: Substrate having a hydrophobic surface
according to the invention with a silica
sublayer deposited by magnetron
sputtering

5

(a) Formation and characterization of the hard silica
layer

10 This example relates to the grafting of fluorosilane
onto an SiO_2 sublayer formed by reduced-pressure
magnetron sputtering.

Three types of SiO_2 were produced:

- 15 - SiO_2 under a pressure of 200 Pa (2 μbar); Ar
flow rate: 15 sccm; O_2 flow rate: 12 sccm;
- SiO_2 under a pressure of 400 Pa (4 μbar); Ar
flow rate: 27 sccm; O_2 flow rate: 12 sccm;
- SiO_2 under a pressure of 800 Pa (8 μbar); Ar
flow rate: 52 sccm; O_2 flow rate: 15 sccm.

20

The plasma was ignited by increasing the DC power from
0 to 2000 W at a rate of 20 W/s.

25 A presputtering operation consisted in applying, for 3
minutes, a 40 kHz pulsed DC power of 2000 W with 4 μs
between the pulses.

A target containing 92% silicon and 8% aluminum was
sputtered.

30

To obtain a 100 nm SiO_2 coating in one pass, the run
speed of the substrate beneath the target was:
5.75 cm/min (200 Pa/2 μbar), 5.73 cm/min (400 Pa/4 μbar)
and 5.53 cm/min (800 Pa/8 μbar).

35

The hardness of the 200 Pa (2 μbar) and 800 Pa (8 μbar)
magnetron SiO_2 layers was measured as described in the
case of the PECVD SiO_2 layers above: measurement of the

haze (in %) during a Taber abrasion test (ISO 3537),
Airco rating.

The results are given in Table 5 below.

5

Table 5

Measured abrasion state:		Taber revolutions			
		50	100	200	300
Haze (%)	SiO ₂ -200 Pa	0.55	0.86	1.35	1.48
	SiO ₂ -800 Pa	0.68	0.99	1.48	1.69
Airco	SiO ₂ -200 Pa	7.84	7.87	7.48	7.3
	SiO ₂ -800 Pa	8.02	7.84	7.12	6.94

10 These SiO₂ layers produced by magnetron sputtering were
hard layers.

(b) Plasma treatment

15 Magnetron-deposited (400 Pa/4 μ bar and 800 Pa/8 μ bar)
silicas were plasma-etched (230 W/300 s) as follows:

- 1) SiO₂ (400 Pa/4 μ bar): 30%-70% SF₆ at
9.99 Pa/75 mTorr;
- 2) SiO₂ (800 Pa/8 μ bar): a) 20% O₂/80% C₂F₆ at
26.66 Pa/200 mTorr; b) 50% O₂/50% C₂F₆ at
20 26.66 Pa/200 mTorr.

(c) Fluorosilane application

25 The procedure was as described at (c) of Example 1.

Five specimens were subjected to various tests, as
described below:

I SiO₂ (400 Pa/4 μ bar) sublayer plasma treated
according to 1) above and then the fluorosilane wiped
30 on in order to graft it (as described above);

II SiO₂ (400 Pa/4 μ bar) sublayer with no plasma
treatment and the fluorosilane wiped on, upon leaving

the magnetron line for preparing the SiO₂;

III SiO₂ (800 Pa/8 μbar) sublayer plasma treated according to 2a) above and then the fluorosilane wiped on;

5 IV SiO₂ (800 Pa/8 μbar) sublayer plasma treated according to 2b) above and then the fluorosilane wiped on; and

V SiO₂ (800 Pa/8 μbar) sublayer with no plasma treatment and the fluorosilane wiped on, upon leaving
10 the magnetron line for preparing the SiO₂.

The results are given in Table 6 below.

Table 6

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Specimen	Etched thickness (mm)	Water detachment volume (μl)		μ _{water} (°)				% haze
		at 45°	at 90°	Initial	Opel (5000 cycles)	Taber (1000 rev.)	NSS (3 wk.)	
I	25	24	14	109.5	101.6	92	108.3	1.09
II				110.4	102.9	92.3		
III	25	24	13	110.3	102.9	95	108.2	
IV	56	23	13	111.1	106.7	90.6	107.1	
V				111	101.4	88.7		

This table shows the very high performance in general, and especially that of test III in the Taber test and test IV in the Opel friction test.

20

EXAMPLE 3

The purpose of this example is to compare four hydrophobic glasses:

25 VI specimen prepared according to Example 5b of

EP 799 873 B1;

VII magnetron-deposited SiO_2 (800 Pa/8 μbar) sublayer (Example 2) plasma treated with 70 sccm of SF_6 , 30 sccm O_2 at 9.99 Pa/75 mTorr, 230 W, 300 s, the fluorosilane being wiped on;

VIII magnetron-deposited SiO_2 (400 Pa/4 μbar) sublayer (Example 2) plasma treated with 50 sccm of C_2F_6 , 50 sccm at 26.66 Pa/200 mTorr, 230 W, 300 s, the fluorosilane being wiped on; and

IX fluorosilane application by wiping on, upon leaving the magnetron-deposited (800 Pa/8 μbar) silica production line.

Various tests were carried out on the specimens thus formed, and the results are given in Table 7 below.

Table 7

Specimen	μ_{water} ($^{\circ}$)				% degraded area ($\mu_{\text{water}} < 60^{\circ}$)
	Initial	Taber (100 revs.)	Opel (5000 cycles)	AWR (50 000 cycles)	
VI	109.6	88.4	104.7	104.8	1.0
VII	111.8	93	103.5	105.0	0.0
VIII	112.5	101.7	104.8	96.0	1.5
IX	112.2	86	108.1	96.4	5.5

The percentage of degraded area ($\mu_{\text{water}} < 60^{\circ}$) was assessed after 50 000 AWR cycles.

Specimens VI to IX that had undergone 50 000 AWR cycles were subjected to an NSS test in the case of some of them and to a QUV test in the case of the others.

The results are given in Table 8 below.

Table 8

5

Specimen	$\mu_{\text{water}} (^{\circ})$						
	NSS				QUV		
	Number of days				Number of hours		
	0	3	20	50	0	1431	3187
VI	105.8	64.1	25.0		99.0	89.0	87.0
VII	106.9	106.6	105.1	99.4	96.0	99.0	87.0
VIII	99.7	95.7	89.4	84.8	92.0	71.0	61.0
IX	97.8	99.8	90.5	84.1	96.0	79.0	65.0

This shows the remarkable performance of specimen VII in the combined AWR/NSS and AWR/QUV tests.

10 Specimens VIII and IX are slightly inferior to VII in the AWR/NSS test combination and substantially inferior in the AWR/QUV combination, while still being at a high level, unknown before the implementation of the invention.

15

EXAMPLE 4

This example describes a particular treatment of the magnetron-deposited (800 Pa/8 μ bar) SiO₂ sublayers.

20

This treatment comprised:

(1) Five minutes, treatment in Ar (80 sccm, 19.98 Pa/150 mTorr), 200 W (35 V bias voltage) in order to reduce any residual roughness;

25

(2) Flash surface treatment: duration \leq 60 s (= 60 s in this example), C₂F₆, SF₆, O₂, H₂;

(3) Fluorosilane application by wiping.

Specimens X to XV are described below by the

characteristics of their treatment step (2):

X: 26.66 Pa/200 mTorr, 230 W, 50 sccm C₂F₆,
50 sccm O₂;

XI: as X, except 100 sccm C₂F₆;

5 XII: as X, except 70 sccm SF₆ and 30 sccm O₂;

XIII: 9.99 Pa/75 mTorr, 203 W, 100 sccm SF₆;

XIV: 7.99 Pa/60 mTorr, 230 W, 100 sccm O₂; and

XV: 13.33 Pa/100 mTorr, 230 W, 75 sccm H₂.

10 The amount of grafted fluorine [F] was determined by
electron microprobe, and then an Opel friction
resistance test was carried out. The results are given
in Table 9 below.

15 Table 9

Specimen	Etched thickness (nm)	Grafted fluorine (μg/cm ²)	μ _{water} (°C)		
			Initial	Opel (5000 cycles)	Opel (15 000 cycles)
X	10	0.9	109.3	102	93.9
XI	< 5	0.4	104.1	105.5	103.3
XII	16	0.8	110.6	103.7	93.6
XIII		0.4	105	104.6	100
XIV	< 5	0.3	106.9	103	101.8
XV	< 5	0.4	111.9	103.9	103.3

These results show that the friction resistance is not
directly correlated with the amount of grafted
20 fluorine, or with the roughness of the sublayer (since
the etched thicknesses do not exceed 16 nm, the
increase in roughness generated by the etching process
is in this case negligible). However, the fluorine
grafting mode plays a role that depends on the surface
25 treatment.

The invention has been described using the word

"substrate". It should be understood that this substrate may be a bare substrate, but it may also be a substrate already provided with functionalities other than the rain-repellent functionality, in particular
5 thanks to layers, and, in certain cases, the sublayer according to the invention may then already form part of the layers that provide these other functionalities.